

# KINETICS OF COAL LIQUEFACTION AT VERY SHORT REACTION TIMES

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## INTRODUCTION

The direct liquefaction of coal is a complex combination of physical and chemical processes. Initially, extractable material is removed from the coal by the process solvent in an amount that depends upon the coal and the solvent characteristics at the temperature of the process. In the subsequent chemical processes, chemical bonds are cleaved thermally or catalytically to form lower molecular weight products. In competition, bond forming (retrograde) reactions of the coal and coal liquefaction intermediates lead to high molecular weight products. These products can foul catalysts, plug the reactor system, and otherwise obscure the underlying chemical fundamentals. This motivated the investigation of the coal liquefaction process at very low conversions, where secondary and retrograde reactions are minimized and the initial liquefaction products can be isolated and studied. This also permits changes in the still solid but partially reacted coal to be investigated.

The study of coal liquefaction under the typical process conditions of high-temperature and high-pressure requires relatively massive equipment. Such equipment has a high heat capacity and is therefore slow to heat up and cool down. This makes a kinetic study at very low conversion quite difficult. To avoid these problems, a special Short Contact Time Batch Reactor (SCTBR) (1-3) was devised which allows the heat up of the process stream to reaction temperature in less than 1 second. The removal and quenching of the reaction products occurs in a similar time period. This paper presents the results of coal liquefaction kinetic experiments with Illinois #6 coal in this novel equipment.

## EXPERIMENTAL

**Apparatus and Operation.** The reactor system, which has been described previously (1-3), is shown in Figure 1. The reactor itself is constructed of 3/4" stainless steel tubing of approximately 12" in length with a wall thickness of approximately 0.433". The preheater and precooler consist of 21 feet of coiled stainless steel tubing with a wall thickness of 0.035".

In operation, both the empty preheater and the reactor are immersed in a sand bath and brought up to the desired reaction temperature prior to the start of the liquefaction reaction. Using high pressure gas, the reaction mixture is driven into the reactor from a small blow case through the preheater. The temperature of the reactants (ca. 30 ml), initially at ambient temperature, approaches the desired reaction temperature to within 5 - 8 °C in approximately 0.3 sec. It reaches the full reaction temperature within 30 seconds. The temperature in the reactor remains quite constant (within  $\pm 2$  °C) throughout the liquefaction experiment. The rapid heat up and stable temperature profile are due to both the small quantity of the reaction mixture relative to the massive reactor and the turbulent flow of the reactants through the preheater.

The liquefaction mixture in the reactor is agitated by gas bubbles introduced from the bottom of the reactor. The degree of agitation is controlled by both regulating the exit gas flow rate from the top of the reactor and the configuration of the gas orifices. A small water cooled condenser is situated above the reactor with a disengaging space above it before the let-down valve to prevent the loss of volatile products from the system and to improve operability.

At a preselected time, the contents of the reactor are driven from the reactor through a precooler into the product receiver with high pressure gas. The total contents of the reactor are not recovered in the receiver (usually only 80 - 90 %) due to the wetting of the walls of the system, and the conversion and other kinetic data are determined by analysis of aliquots.

**Product Work-up.** The liquefaction products were separated into liquid and partially reacted solids by filtration through a sintered glass filter, and the liquids and solids were analyzed separately. The liquids were bottled and nitrogen blanketed for subsequent analysis. The solids were washed with fresh tetralin (to remove residual coal liquids) and then methylene chloride to remove any tetralin remaining. The washed solids were dried in a vacuum oven at 105°C for 48 hours.

**Determination of Percent Conversion.** During coal liquefaction, the mineral matter (which is insoluble in tetralin) remains with the partially reacted solid coal and does not go into the liquid (4). When the liquefaction is carried out without catalyst, this provides a means of measuring the conversion of the coal to liquid product by the ash content of the solid residue. The ash content is determined by TGA, and provides the conversion as shown in Eq. 1:

$$\text{Conversion} = (1 - \frac{X_0}{X}) \times 100 \quad (\text{wt}\%) \quad (1)$$

In Eq. 1,  $X_0$  and  $X$  are the ash contents of a control sample and the coal liquefaction residue, respectively. The control sample is the original coal, which is processed exactly as a liquefaction residue except at room temperature. Multiple experiments have shown that the ash content can be determined by TGA with a standard deviation of 0.1%.

When the liquefaction is carried out in the presence of an inorganic catalyst, the conversion calculation must include an ash value corrected for the ash derived from the catalyst.

**Catalysts Used.** Sulfided molybdenum naphthenate has been the principal liquefaction catalyst used to date. This catalyst has been prepared by dissolving molybdenum naphthenate in tetralin and reacting the solution with methyl disulfide. That this catalyst is only active for liquefaction in the presence of hydrogen is shown in Table 1.

Table 1 Catalysis of coal liquefaction by molybdenum naphthenate (Illinois #6; 8 of T/C; 390 °C; 5 min.)

molybdenum naphthenate g	methyl disulfide g	Mo wt%	Conversion wt%
under 1000 psig nitrogen gas			
0.00	0.00	0.00%	28.1%
0.00	1.03	0.00%	27.5%
0.59	0.00	0.85%	28.0%
0.62	1.07	0.86%	28.4%
under 1000 psig hydrogen gas			
0.00	0.00	0.00%	33.8%
0.00	1.03	0.00%	32.3%
0.61	0.00	0.87%	33.5%
0.61	1.15	0.87%	41.8%

Without sulfidation, the molybdenum naphthenate itself is inactive, as is the sulfiding agent.

**TGA Methods.** A typical TG curve and its differential (DTG) for unreacted Illinois #6 bituminous coal at 10°C/min heating rate and 100 ml/min nitrogen gas sweep are shown in Figure 2. The TG curve (solid line) shows a small drop below 200 °C due to loss of moisture. In the neighborhood of 350 - 400 °C, a large loss of weight is observed. When the weight loss has leveled off at 950°C, the temperature is held for 7 minutes. This loss in weight is designated as "Volatile Matter". After oxygen is then introduced, another large drop in weight, designated "Fixed Carbon", follows to a steady weight representing the "Ash Content". The Volatile Matter, Fixed Carbon, and ash

are important parameters to follow during the liquefaction process.

The DTG curve is also of interest since it clearly shows the volatilization processes occurring during the TG analysis. This DTG curve changes very significantly during the liquefaction process as shown in Figure 3.

## RESULTS AND DISCUSSION

Figure 4 shows conversion vs time curves for Illinois # 6 coal in nitrogen and in hydrogen in the absence of a catalyst at 390°C. The initial conversion in the first minute is due to the physical extraction of a soluble fraction of the coal into the tetralin, which occurs in both a nitrogen and a hydrogen environment. This is followed by an induction period and then the slow conversion of the coal structure to liquid product. As the liquefaction temperature is increased (Figure 5), the amount of extraction increases and the induction period becomes shorter. In the absence of a catalyst, however, increases in temperature above about 408°C result in little increase in soluble product. The reason for this can be found in the TG analysis of the residue. The rate of removal of Volatile Matter increases steadily as the temperature increases (Figure 6a), regardless of whether the system is in hydrogen or nitrogen. However the Fixed Carbon increases at a very rapid rate above 408 °C (Figure 6b). This is the retrograde process which results in low liquid yields and the formation of tar and coke.

Figure 7 summarizes the conversion vs time for liquefaction of Illinois #6 in

hydrogen at 390°C in the presence of about 1% sulfided molybdenum naphthenate in tetralin. A rapid extraction is again observed in the first minute, followed by the induction period. The subsequent conversion is faster than is observed for the uncatalyzed liquefaction. Figure 8 shows the content of Fixed Carbon in the residue as a function of time. The retrograde process is very significantly reduced. The precursors to the retrograde reactions are apparently being hydrogenated in the presence of hydrogen and the catalyst.

#### SUMMARY AND CONCLUSIONS

- 1). In the first minute of the liquefaction process, in the presence or absence of a catalyst, and in hydrogen or nitrogen, there is a very rapid conversion to liquid product (approximately 25 - 30 % for Illinois #6 coal) due to the extraction of tetralin-soluble material from the coal into the liquid phase.
- 2). The initial conversion is followed by an induction period and then a slower conversion, presumably of the coal structure itself, which represents the breaking of chemical bonds. This is more rapid in the presence of a sulfided molybdenum naphthenate catalyst.
- 3). At higher temperatures, the degree of extraction is higher and the induction period shorter. However, in the absence of hydrogen and a catalyst, the breakdown of the coal structure into coal liquid is offset by the build up of retrograde products.

#### ACKNOWLEDGEMENTS

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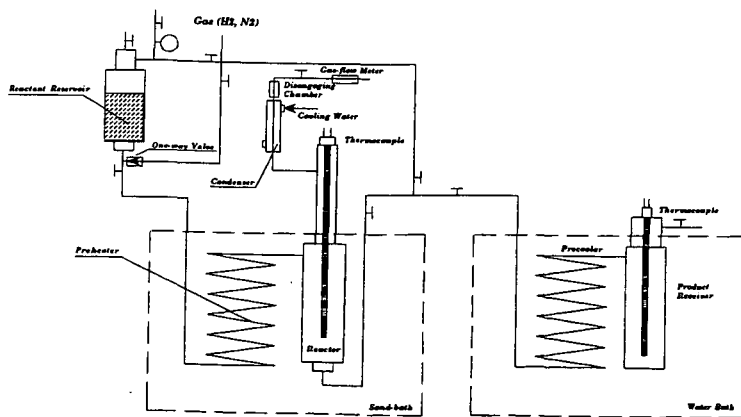


Figure 1 SCTBR system for studying direct coal liquefaction from the initial stages

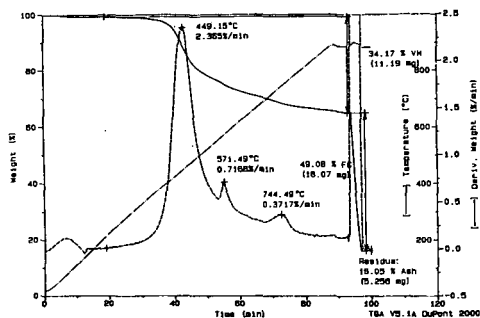


Figure 2 A TG scan on the Illinois #6 coal at 10 °C/min

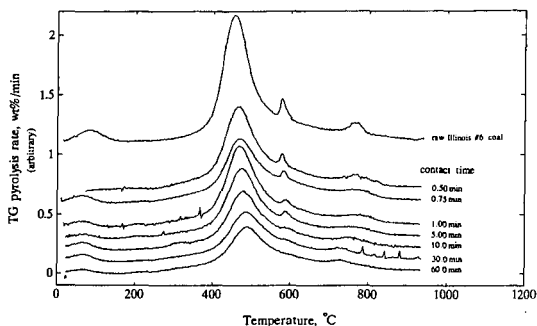


Figure 3 DTG profiles for residues of the Illinois #6 coal after liquefaction in tetralin at the selected contact times (TG scan at 10 °C/min; Liquefaction run at 390 °C under 1000 psig  $N_2$ )

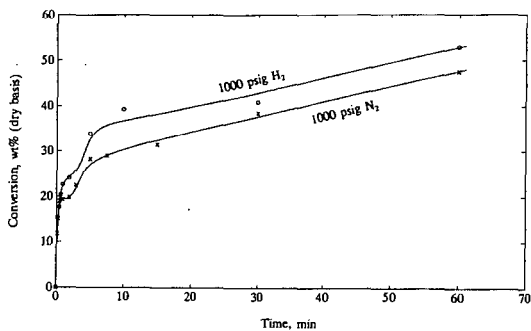


Figure 4 Liquefaction conversion of the Illinois #6 coal at 390 °C

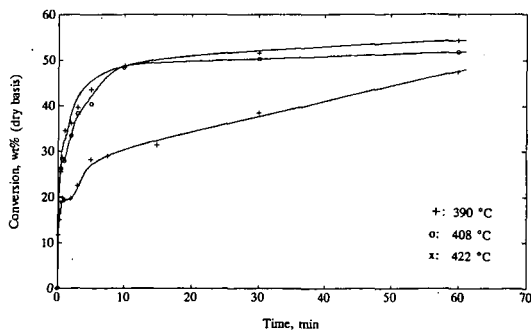


Figure 5 Kinetics of the Illinois #6 coal liquefaction in tetralin under 1000 psig  $N_2$

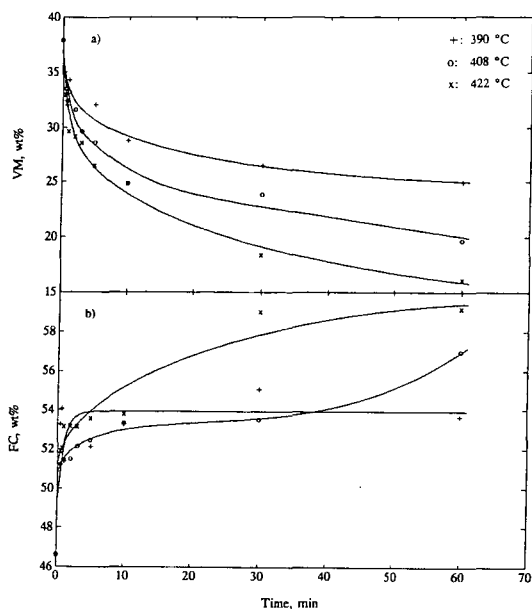


Figure 6 VM (volatile matter) (a) and FC (fixed carbon) (b) in liquefaction residues determined by TGA (Liquefaction: Illinois #6 coal, T:C = 8:1, 1000 psig  $N_2$ ; TGA: 100  $cm^3$ (STP)/min  $N_2$ , 100 °C/min)

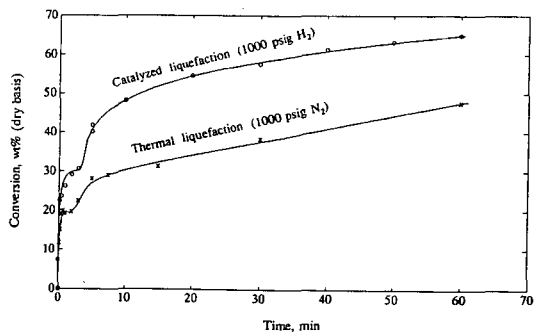


Figure 7 Conversion of the Illinois #6 coal in the thermal and catalyzed liquefaction at 390 °C (Catalyst: ca. 0.9 wt% molybdenum naphthenate; T:C = 8:1)

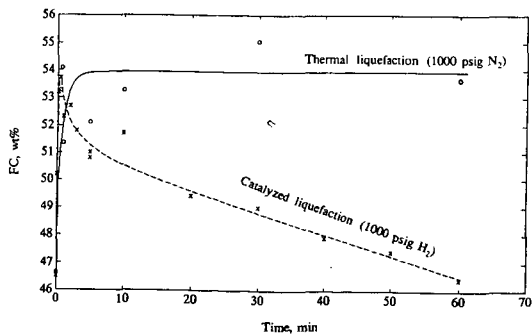


Figure 8 FC (fixed carbon) in liquefaction residues determined by TGA (Liquefaction: Illinois #6 coal, 390 °C, T:C = 8:1; TG scan: 100  $cm^3$ (STP)/min  $N_2$ , 100 °C/min)